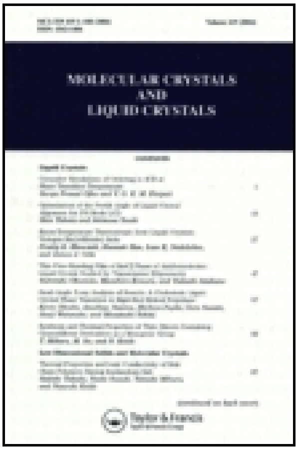

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MOLECULAR WOBBLING MOTION IN LANGMUIR FILMS BY TIME-RESOLVED FLUORESCENCE DEPOLARIZATION METHOD

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Abstract Molecules in a Langmuir film are wobbling in the time range of nanosecond. The wobbling motion of β-DPH HPC assembled as Langmuir films were measured by time-resolved fluorescence depolarization method. Using "double cone model", it was found that the angular range and the velocity of the motion decreased with increasing of the density of the molecules in the Langmuir films.

INTRODUCTION

Structure and stability of organized molecular films must depend on the molecular motion on the analogy of biological membranes. Thus, in order to design the organic molecular devices using Langmuir-Blodgett films, study of the molecular motion and the dynamic structure of the film becomes very important. It is also necessary to study molecular motion in Langmuir films appeared prior to the Langmuir-Blodgett film formation.

In this work, we measured the molecular motion of Langmuir films by time-resolved fluorescence depolarization method.[1] We will analyze angular ranges and velocity of the molecular wobbling motion depending on the molecular density in the films.

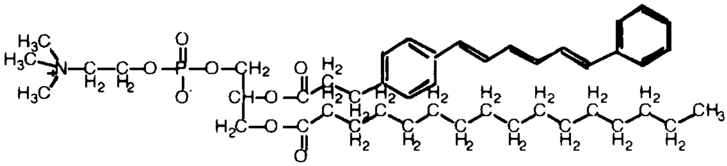


FIGURE 1 β -DPH HPC

METHOD

Langmuir films used were composed of β-DPH HPC (2-(3-(diphenylhexatrienyl) propanoyl)-1-hexadecanoyl- *sn*- glycero-3-phosphocholine, Fig.1) (Molecular Probes Co. Ltd., U.S.A.) on a small size trough (48mm × 19mm) filled with distilled water. Surface pressure-area isotherms of this

Langmuir film was measured by a moving wall type LB system (Nippon Laser & Electronics Lab., LB-150MW).

An argon ion laser (COHERENT, INNOVA 100-15) and a dye laser (COHERENT, Model 700) with a cavity dumper (COHERENT, Model 7200) were employed as a pulsed light source. The light was polarized to the horizontal direction. Decay curves of polarized fluorescence of β-DPH HPC films excited with the pulsed laser were obtained by the time-correlated single photon counting technique (Fig. 2).[2]

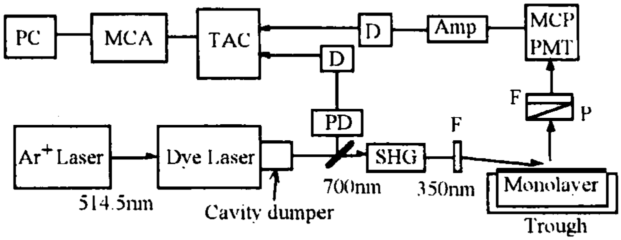


FIGURE 2 Block diagram of time-resolved fluorescence mesurement system. (P : Polarizer, F: Filter, PD : Photo Diode, D : Discriminator)

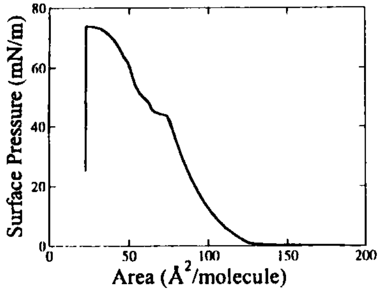
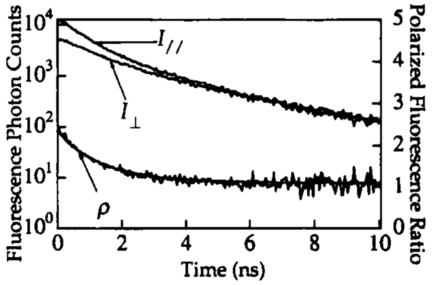


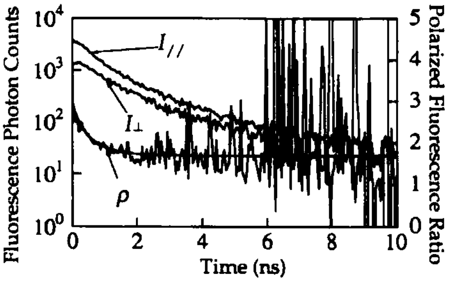
FIGURE 3 Surface pressure-area isotherm of β-DPH HPC Langmuir film

RESULTS

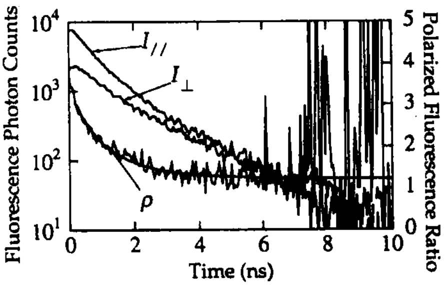
Figure 3 shows a surface pressure-area isotherm of a Langmuir film of β-DPH HPC.



(a) A = 198 Å^2/molecule



(c) A = 99 Å^2/molecule



(b) A = 132 Å^2/molecule

FIGURE 4 Decay curves of polarized fluorescence and ratios of them at A = (a)198 , (b)132 and (c)99 Å^2/molecule. Smooth solid lines overlapping ρ (t) are fitting curves calculated using "double cone model" (see DISCUSSION section).

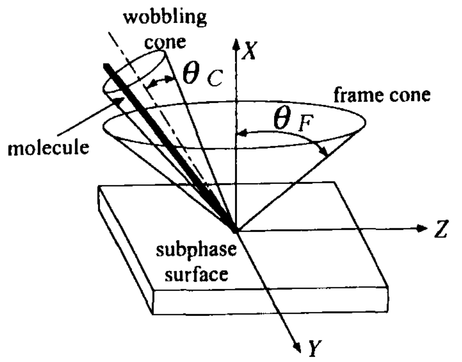
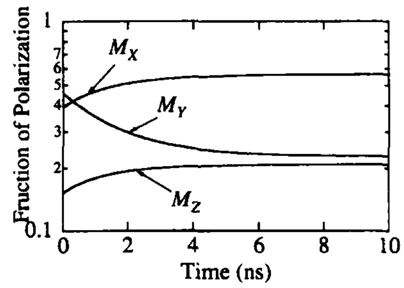


FIGURE 5 Double cone model

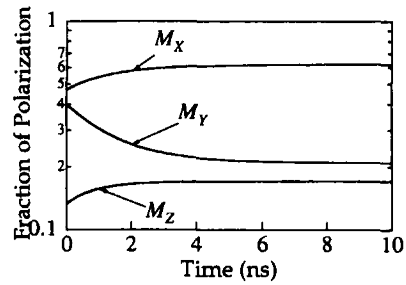
The time-resolved fluorescence depolarization measurement was performed for the film at three different molecular density. This density is usually expressed as the area occupied by one molecule (A, Å^2/molecule).

Figure 4 (a)-(c) shows decay curves of polarized fluorescence of the Langmuir films at A= 198, 132 and 99Å^2/molecule, respectively. The polarization direction of $I_{//}(t)$ was parallel to that of excitation light and $I_\perp(t)$, perpendicular.

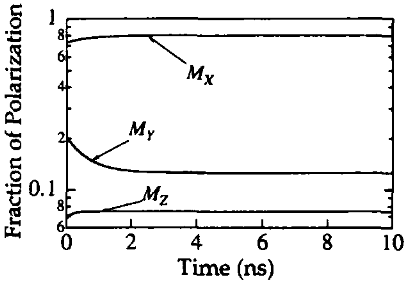
The time courses of fluorescence decay depend on the fluorescence life time and the depolarization rate by the change of angular distribution of molecules. In order to concentrate on the fluorescence depolarization, we calculated polarized fluorescence intensity ratio, $\rho(t) = I_{//}(t)/I_\perp(t)$. The value of $\rho(t)$ just after the excitation was near two and then $\rho(t)$ decayed within several nanoseconds giving final limiting value. As the density of molecules increased, the final value and the relaxation time of $\rho(t)$ decreased.



(a) A = 198 Å^2/molecule



(b) A = 132 Å^2/molecule



(c) A = 99 Å^2/molecule

FIGURE 6 Fraction of polarization by fitting analysis at A = (a)198 , (b)132 and (c)99 Å^2/molecule.

DISCUSSION

In order to realize the relation between the dynamic structure and the molecular packing of the film, we evaluated the angular range and the velocity of the molecular wobbling motion using double cone model shown in Fig. 5. This model is an expansion of the "wobbling in cone model[3]". This model has two kinds of virtual cone, a "wobbling cone" (a semiangle of the cone is θ_C called "wobbling angle") and a "frame cone" (a semiangle of the cone is θ_F called "distribution angle"). The molecules are wobbling only inside the wobbling cone, and the wobbling cones distribute in the frame cone. A velocity of the wobbling motion is measured by wobbling diffusion constant D_W.

When the parameters θ_C, θ_F and D_W are determined, one can obtain the initial value (M_Ξ^0), the final value (M_Ξ^∞) and relaxation time (σ_Ξ) of "fraction of polarization" where $\Xi = X$, Y or Z. $M_\Xi(t)$ is calculated as

$$M_\Xi(t) = (M_\Xi^0 - M_\Xi^\infty)\exp(-\frac{t}{\sigma_\Xi}) + M_\Xi^\infty . \qquad (1)$$

Y-axis is parallel to the direction of polarized excitation light and Z-axis is parallel to the normal of the subphase surface, in this work. In the coordinate system, $\rho(t)$ is calculated as $\rho_C(t) = M_Y(t)/M_Z(t)$. Thus, we can obtain the value of θ_C, θ_F and D_W by fitting $\rho_C(t)$ to the measured $\rho(t)$. Figure 6 (a)-(c) shows the results of the fraction of polarization obtained by the procedure. And $\rho_C(t)$ are shown as smooth line overlapping $\rho(t)$ in Fig. 4.

Table I lists θ_C, θ_F and D_W of the Langmuir films for three different samples, using above procedure. When the area becomes small, θ_C, θ_F and D_W become small. It indicates that the wobbling motion of molecules in tightly-packed film is more restricted than that in loosely-packed one.

TABLE I Area dependence of wobbling angle, distribution angle and wobbling difusion constant

Area (A^2/molecule)	θ_C (degree)	θ_F (degree)	D_W (rad^2/ns)
99	20	30	0.05
132	40	40	0.07
198	50	40	0.08

CONCLUSION

Molecular wobbling motion in Langmuir films could be observed by the time-resolved fluorescence depolarization technique. As the density of molecules increased (198→99Å^2/molecule), the angular ranges and the velocity of the motion decreased (θ_C : 50°→20°, θ_F : 40°→30°, D_W : 0.08rad^2/ns→0.05rad^2/ns).

REFERENCES

1. J.R.Lakowicz, Principles of fluorescence spectroscopy (Plenum, New York, 1983), Chapter 6.
2. K.Mukasa, T.Araiso and N.Kimura, New Functionality Materials, Volume C: Synthetic Process and Control of Functionality Materials (T.Tsuruta, M.Doyama and M.Seno eds.), (Elsevier Science Publishers, Amsterdam, 1993), pp.705-710.
3. K.Kinosita,Jr., S.Kawato and A.Ikegami, Biophys.J., 20, 289 (1977).